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12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		13. ABSTRACT (Maximum 200 words) The birefringence level in a copolymer or a blend containing disperse red 1 acrylate or methacrylate structural units depends not only on the molar fraction of the azo component, but also on the type of the next-neighbor on the chain. Copolymers behave quite differently from blends. Also, if a few azo groups are neighboring each other, the induced birefringence is more stable.	
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Optically Induced Birefringence in Copolymers and Blends Containing Azobenzene Groups

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INTRODUCTION

Azoaromatic (azo) polymers have been shown to exhibit stable, reversible optically induced birefringence and dichroism.¹ It is the purpose of this study to determine the effect of varying the concentration of the azo chromophore, within series of copolymers and blends, on the level of birefringence that can be optically induced within the polymer sample.

MATERIALS

The polymers being studied have the substituted azobenzene group attached as a side chain. The materials discussed in this paper are poly-[4'-[[2-(acryloyloxy)ethyl]ethyl-amino]-4-nitroazobenzene] (PDR1A) and poly-[4'-[[2-(methacryloyloxy)ethyl]ethyl-amino]-4-nitroazobenzene] (PDR1M). The corresponding monomers have been copolymerized with methyl methacrylate (MMA) in varying amounts to produce two copolymer series for study. PDR1A was also blended with PMMA to produce a blend series. Figure 1 gives the structures of the investigated materials.

EXPERIMENTAL

Polymer films were spin cast from tetrahydrofuran (THF) onto a glass substrate. They were then heated briefly to between 60 and 70 degrees C

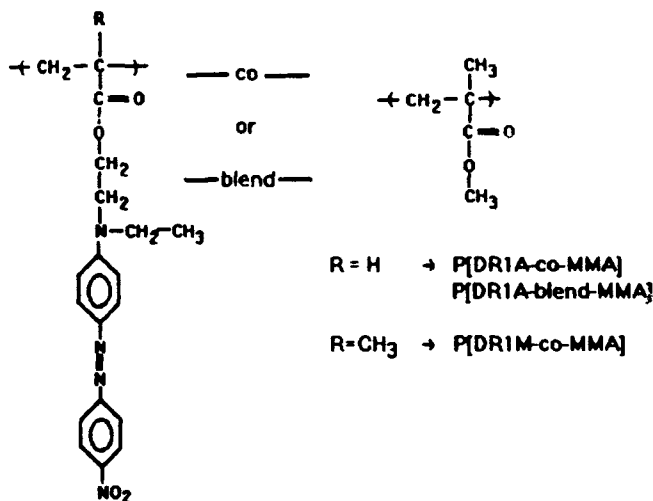


Figure 1 : Polymer structural units.

to drive off any trapped THF, and their thickness measured via interferometry (100 to 500 nm). Birefringent properties were studied by supporting each film between crossed polarizers and using a low power laser of a nonabsorbing wavelength (typically HeNe) as a probe. The film was then irradiated coincidentally with a 10 mW beam from an argon laser ($\lambda=488$ nm), having the polarization state controlled by means of a Pockels cell. When in plane polarized operation, the orientation of the electric field was arranged at an angle of 45 degrees to that of the crossed polarizers. The intensity of the probe beam was monitored and digitally recorded as a function of time.

PROPOSED MECHANISM

The proposed mechanism for the optical behaviour of these polymers under irradiation with an absorbing wavelength involves the selective excitation of the azobenzene groups with respect to their orientation. The probability of exciting an azo bond is proportional to the irradiance times the square of the \cos of the angle between the azo dipole moment and the exciting electric field.² If irradiation is with a plane polarized source, only azo groups with a component of their dipole moment in the polarization plane can be pumped. When excited, the azo group undergoes trans-cis-trans isomerization cycles. During these cycles, the orientation of the azo side group may or may not change, depending on the local environment. Should reorientation occur and result in a smaller component of the dipole moment being oriented in the polarization plane, the probability of exciting this azo group again is reduced. This selective excitation creates a preferential orientation perpendicular to the polarization plane of the pump beam, and hence a net macroscopic anisotropy that will affect the polymer material's optical properties.² The amount of anisotropy will increase with irradiation time until a saturation level is approached, whereupon all achievable reorientation of participating groups has occurred. When irradiation is terminated, the anisotropy thermally relaxes to a stable level.

RESULTS AND DISCUSSION

It was observed that the blends and copolymers have different behavior, both

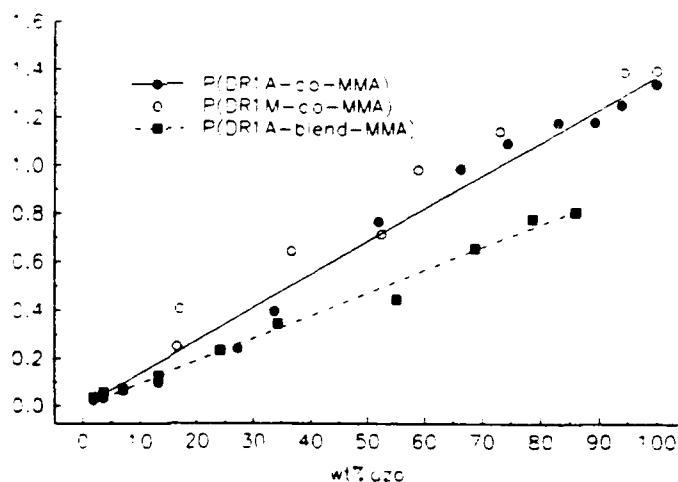


Figure 2 : Absorption coefficient as a function of weight fraction azo structural unit.

in absorption and induced birefringent properties.

The absorption coefficient dependence on the weight per cent azo concentration appears to be linear, as seen in figure 2, however, the slope is different for the blend series in comparison to the copolymers. Figures 3 and 4 show the birefringence induced as a function of azo weight fraction. The relationship for the blend series seems linear for the concentrations used, however, this linearity does not extrapolate to the homopolymer values (100% azo). The behavior for the two copolymer series shows a plateau at midrange concentrations. The absorption behavior of the blend series may be affected by the presence of domains of the homopolymer, or a difference in density (experimental results were calculated using weight fraction instead of volume fraction, the density will have to be determined). It is probable that the plateau region in the copolymers birefringence curves is due to a neighboring group effect. Similar behaviour was reported by Carr *et al* for polarization as a function of concentration and was attributed to dipolar pairing.³

Figure 5 shows the relative fraction of birefringence relaxation with respect to the saturation level, upon termination of irradiation. From these curves it can be seen that relaxation is a function of azo group concentration for the copolymers. The blend curve appears possibly flat indicating less dependence on concentration. The

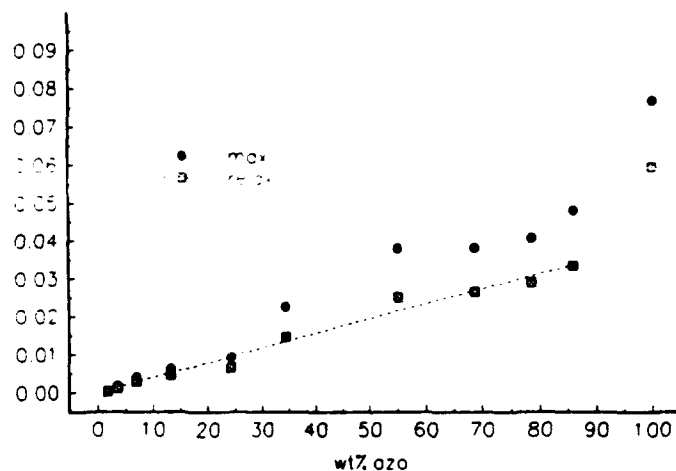


Figure 3 : Blend birefringence as a function of weight fraction azo structural unit.

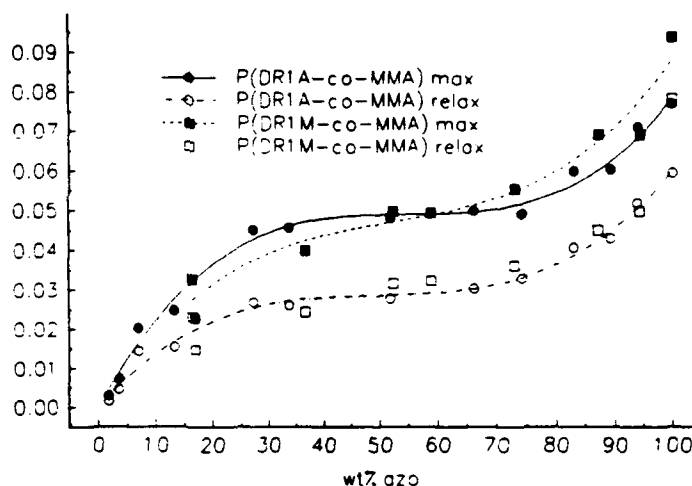


Figure 4 : Copolymer birefringence as a function of weight fraction azo structural unit.

blend series also shows a consistently lower fraction of anisotropy lost in comparison to the copolymers. Values for concentrations of thirty weight percent and lower have been omitted in this graph, because these samples show another temporal effect which we are now investigating.

Also, the time required to achieve saturation increases as the azo concentration increases (for concentrations above thirty weight percent).

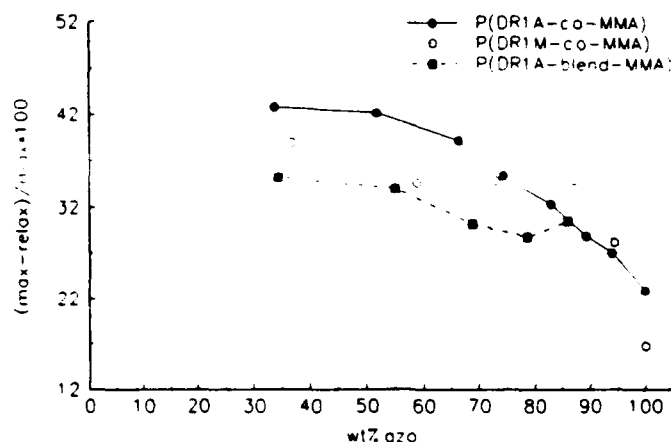


Figure 5 : Birefringence relaxation as a function of weight fraction azo structural unit.

CONCLUSIONS

The absorption and ordering properties of the copolymer and blend series studied differ significantly. At very high azo concentrations in the copolymers the overall birefringence is increased, but at the expense of the amount of time to achieve saturation. The existence of a plateau in the birefringence curves of the copolymers may allow for the design of the absorption properties of a film through a combination of thickness and concentration manipulation, without significantly affecting the level of birefringence.

The optically induced anisotropy is more stable in the blended material than in the copolymers, since the relaxation behaviour appears independent of azo concentration. This would follow from a more consistent molecular environment throughout the blend series.

ACKNOWLEDGEMENTS

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REFERENCES

1. P. Rochon, J. Gosselin, A. Natansohn and S. Xie, *Appl. Phys. Letters*, **60**, 4, (1992).
2. A. Natansohn, P. Rochon, J. Gosselin and S. Xie, *Macromolecules*, **25**, 2268, (1992).
3. P. L. Carr, G. R. Davies, and I. M. Ward, *Polymer*, **34**, 5, (1993).

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